Picking up from where Ian Robinson left off…

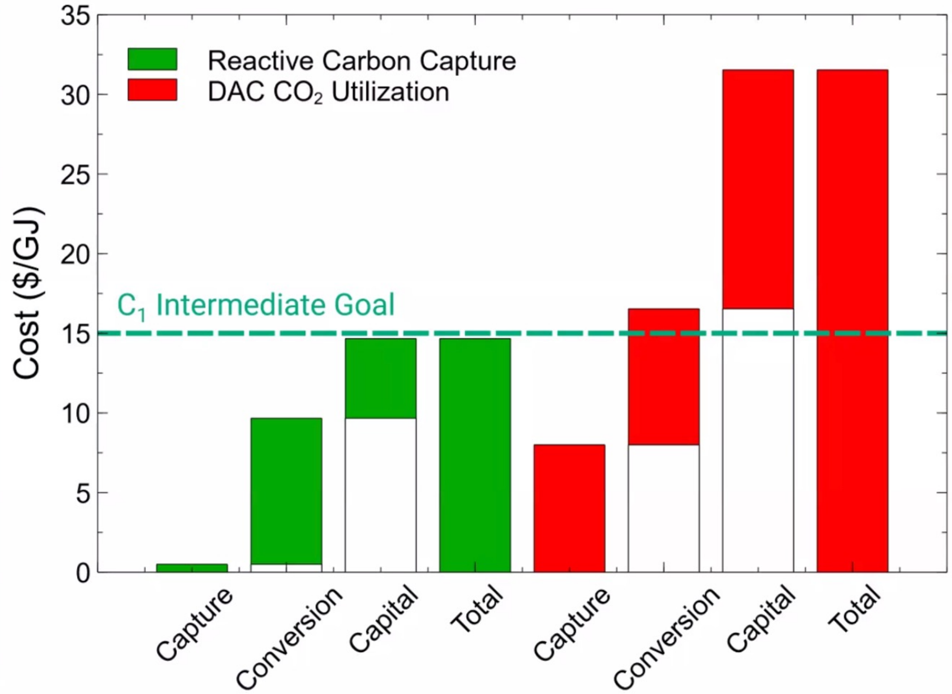
Reactive Carbon Capture Could Produce a Viable Intermediate

Energy Input Conversion Factors:

- \$10/MWh = \$ 2.77/GJ
- \$1/kg H_2 = \$8.20/GJ (LHV)

An Example RCC Pathway Comparison to DAC CO_2U

- \$20/MWh Electricity @ 60% η_{C1}
  - ~ \$9/GJ
- CapEx \$250/t_{CO2}/yr DAC, \$500/kW Electrolyzer
  - ~\$5/GJ
- Capture BOP ~\$0.5/GJ
- Total ~ \$15/GJ



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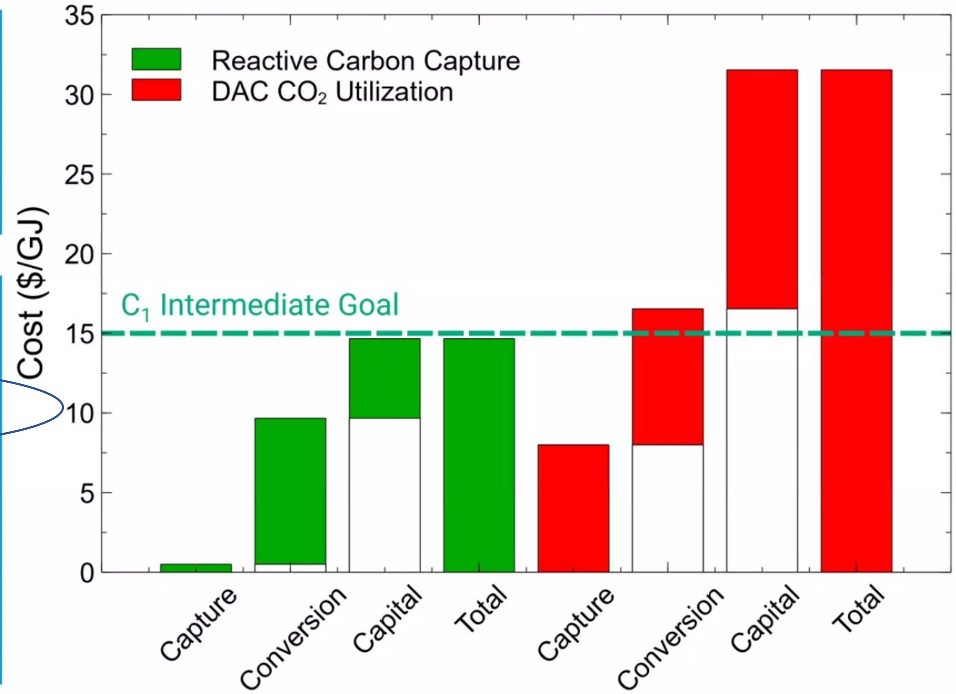

With reactive capture,
we may have
a viable path
at 60%
overall
energy efficiency *if*
**from
capture liquid**

arpa-e CHANGING WHAT'S POSSIBLE

22

\$20/MWhr = \$5.5/GJ
At Energy Efficiency 0.6, this is \$5.5/0.6=\$9/GJ product value

What did the **boldface** mean?

With reactive capture,
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**from
capture liquid**

Include in the energy cost:
- Electrolysis energy
- Separation of desired product from all other components (including any CO_2)
    - And including any crossover (and resultant anodic stream separation) effects

(Don't include cost of contacting CO_2 with capture liquid/sorbent … Ian detailed that separately already…)

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- In reactive capture, we don’t separate out a release-from-capture cost vs. an electroreduction cost – it’s a single cost for electro-release-upgrade
- IF we can keep the CO_2 captured, and if the desired product is released – we can reduce separation costs

Another way to get to the Robinsonian Numbers:

C1 such as CO at \$9/$GJ_{productvalue}$ for energy, hence \$15/ $GJ_{productvalue}$ all in, corresponds to \$15/$GJ_{productvalue}$ *9.2GJ $GJ_{productvalue}$ /ton for CO = \$138/tonCO.

(In my talk I will rely on audience remembering these figures:

9.2 GJ/ton is the LHV of CO

So at Ian's 60% overall energy efficiency, **15 GJ/tonCO** of total energy is budgeted for CO production, **from captured state**)

With this one can make methanol for ~ \$380/ton. A little pricey but right ballpark.

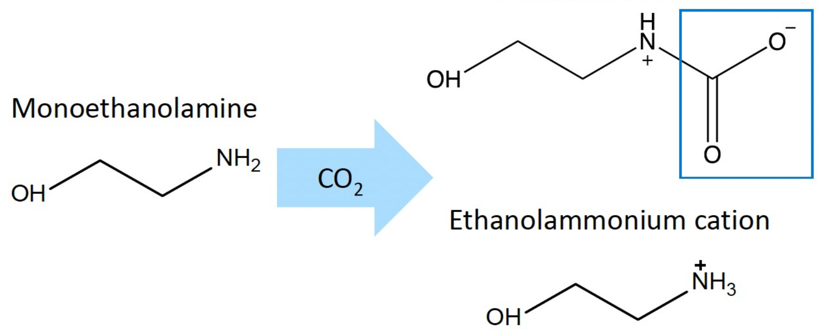
C2 such as C2H4 for \$18/GJ all in corresponds to \$18/GJ*48 GJ/ton = \$860/ton all in. A little pricey but right ballpark.

Direct E-upgrade of CO2 from Capture Absorbent

1. An early attempt at direct e-upgrade of captured CO_2 to CO
2. In this early attempt … how far were we (at small scale) from \$15/GJ? (= 15 GJ/ton)
3. Where would we have to move the metrics to get to \$15/GJ? (= 15 GJ/ton), and how might we approach this?
4. Grand Problems and Questions

1. An early attempt at direct e-upgrade of captured CO_2 to CO

- We worked in monoethanolamine MEA solution which, upon absorption of the CO_2 molecules, turns into:
  - Carbamate anion
    - i.e. the amine-CO_2 adduct, i.e. the reactant
  - Ethanolammonium cations, the supporting electrolyte
- We used an Ag electrocatalyst as cathode
- We formed the catholyte by purging MEA with CO_2, after which we purged with N_2 to remove dissolved CO_2

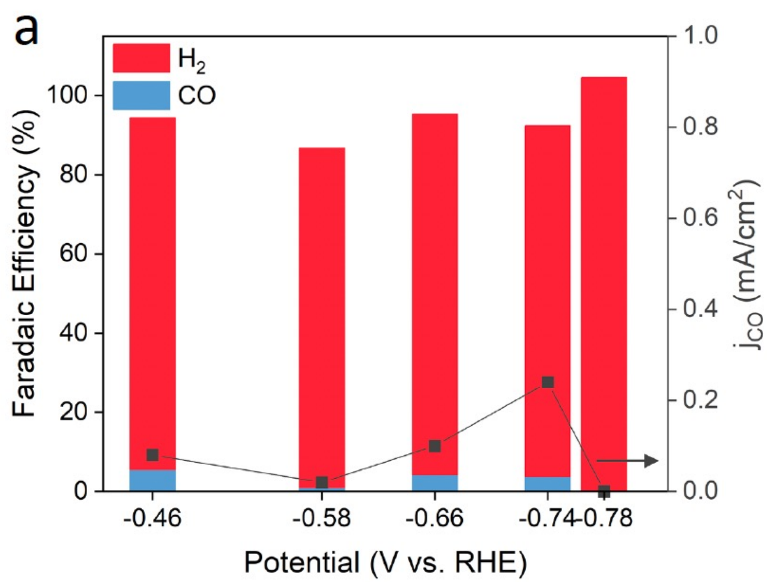


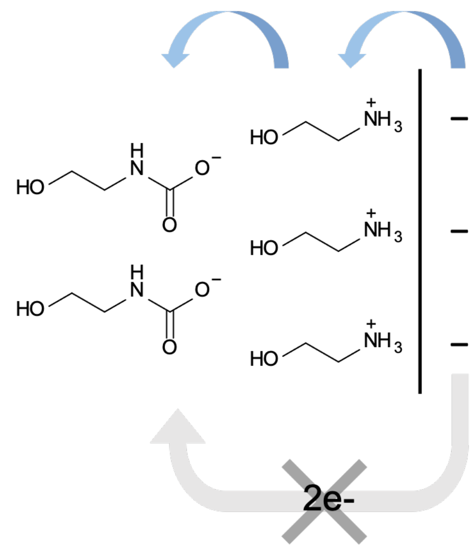
Geonhui Lee, Yuguang C. Li, … Edward Sargent, "Electrochemical upgrade of CO_2 from amine capture solution," Nature Energy, 2021.

1. An early attempt at direct e-upgrade of captured CO_2 to CO

- Unfortunately, the faradaic efficiency to CO was below 5% at all potentials we studied

- We can account for this if the electron transfer between the electrode (electrocatalyst) and the carbamate molecule is inefficient

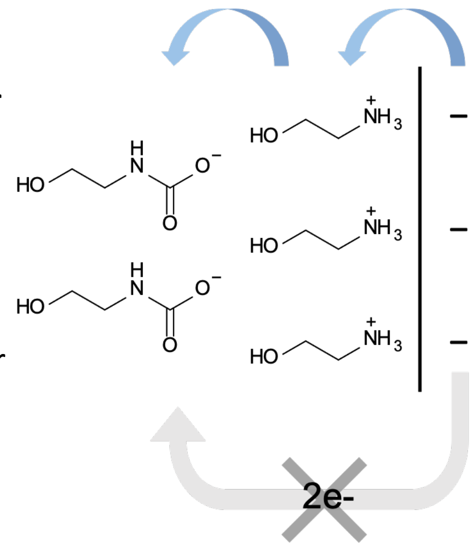




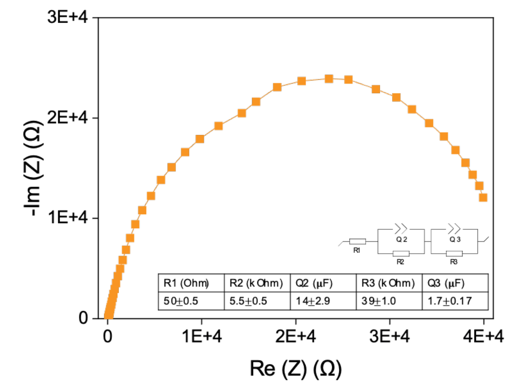
Geonhui Lee, Yuguang C. Li, … Edward Sargent, “Electrochemical upgrade of CO_2 from amine capture solution,” Nature Energy, 2021.

1. An early attempt at direct e-upgrade of captured CO_2 to CO

- We believe that the cationic ethanolammonium ion will occupy the inner Helmholtz layer, the result of the negatively-biased surface
- Thus (see blue arrow), to the extent that electron transfer occurs…
  - It must go first through the ethanolammonium for reaching the carbamate
  - EIS showed two distinct electron transfers



Electrochemical Impedance Spectroscopy

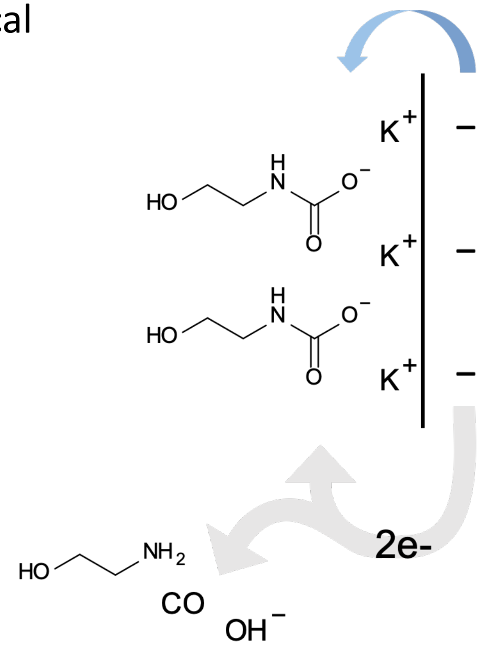


R1 (Ohm)	R2 (k Ohm)	Q2 (μF)	R3 (k Ohm)	Q3 (μF)
50±0.5	5.5±0.5	14±2.9	39±1.0	1.7±0.17

Geonhui Lee, Yuguang C. Li, … Edward Sargent, "Electrochemical upgrade of CO_2 from amine capture solution," Nature Energy, 2021.

1. An early attempt at direct e-upgrade of captured CO_2 to CO

- We therefore tried to tune the electrochemical double layer (EDL) by introducing properly-sized cations
  - Our goal was to disrupt the undesired charge-blocking layer
  - And to pursue direct electron transfer to carbamate
- The figure shows a cartoon of role of introducing alkali cations:
  - EIS now showed a single charge transfer process
  - Surface EDL capacitance shows a more compact double layer – we note that the hydrated K^+ in the EDL, replacing the ethanolammonium cation



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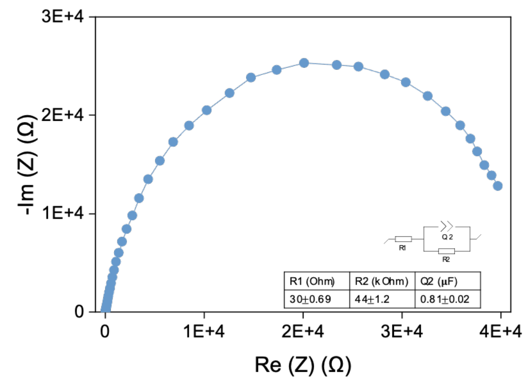
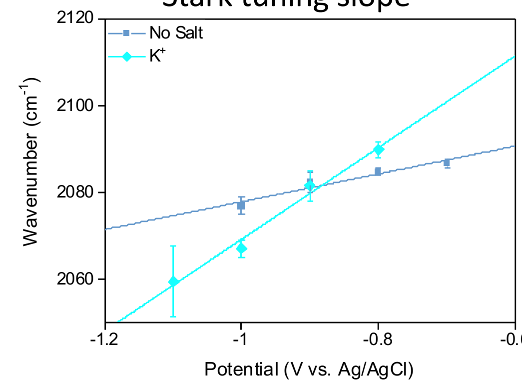


Stark tuning slope



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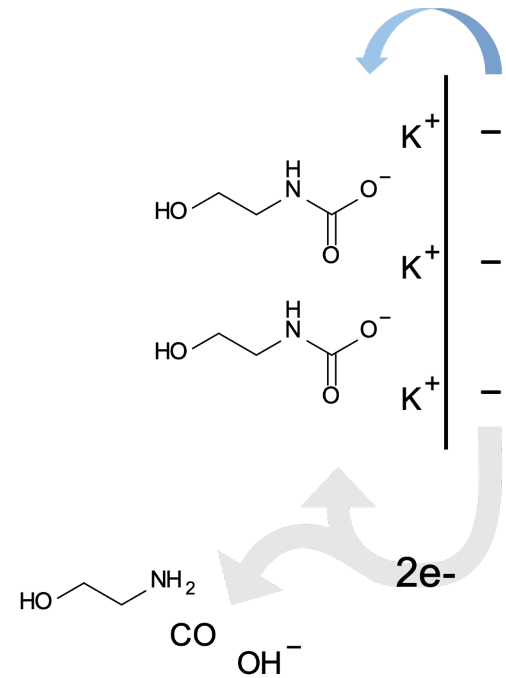


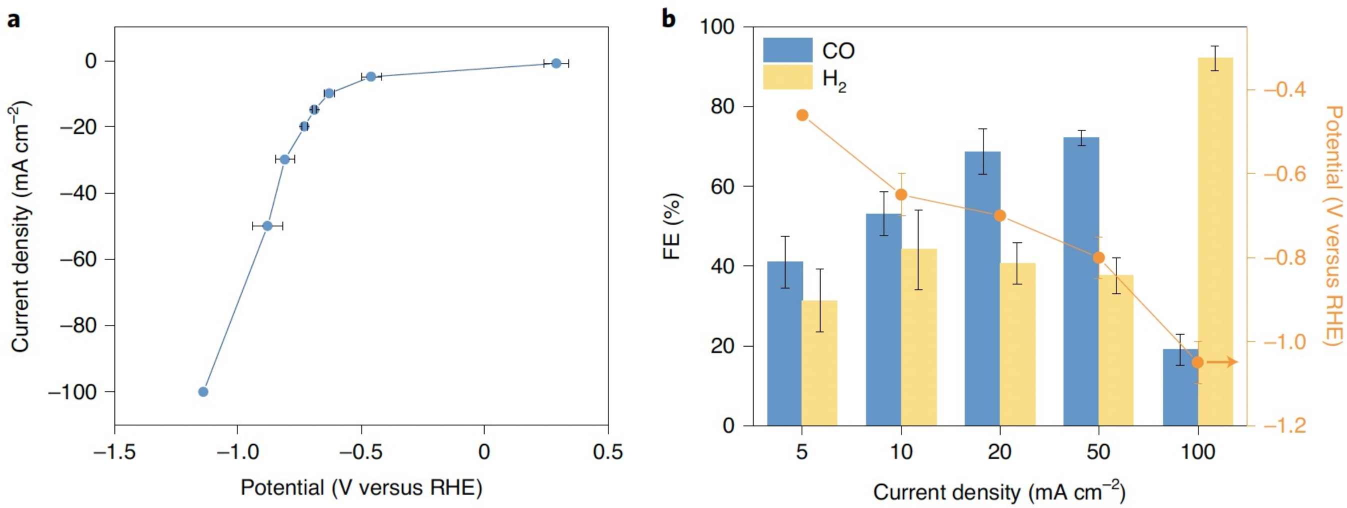
- Under these conditions, the direct electrochemical conversion of amine-CO_2 to CO becomes possible:

$$RNHCOO^- + 2H^+ + 2e^- \rightarrow RNH_2 + CO + OH^-$$

Geonhui Lee, Yuguang C. Li, … Edward Sargent, “Electrochemical upgrade of CO_2 from amine capture solution,” Nature Energy, 2021.

1. An early attempt at direct e-upgrade of captured CO_2 to CO

- We further tailored:
  - Explored libraries of alkali cations
  - Operated at 60ºC
- And achieved:
  - 72% faradaic efficiency
  - 50 mA/cm^2
  - At -0.8 V (vs. RHE)



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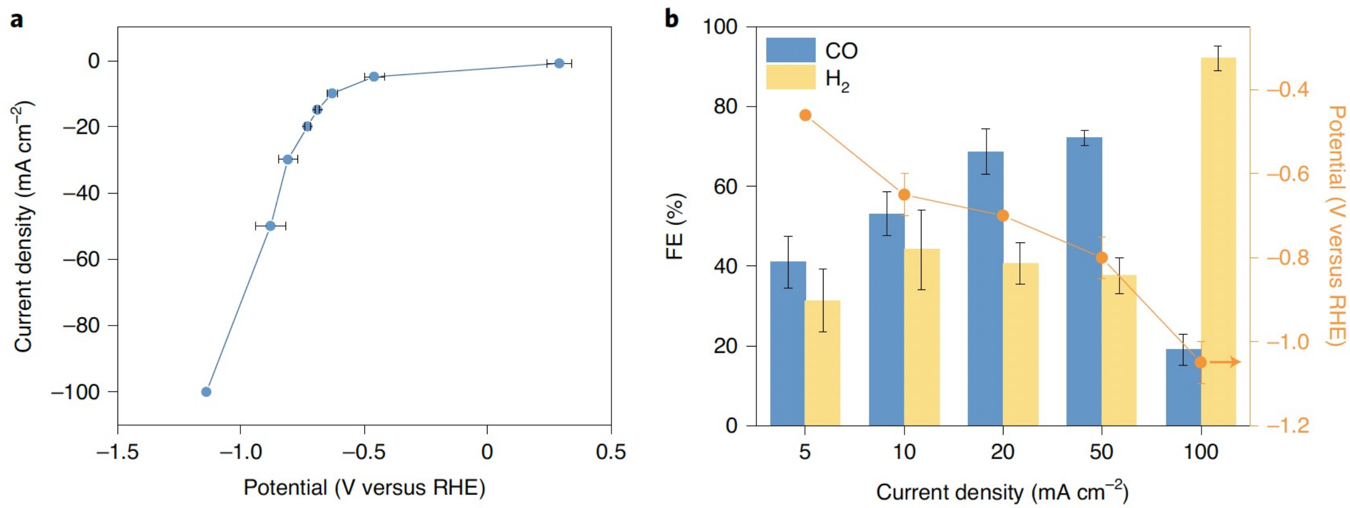
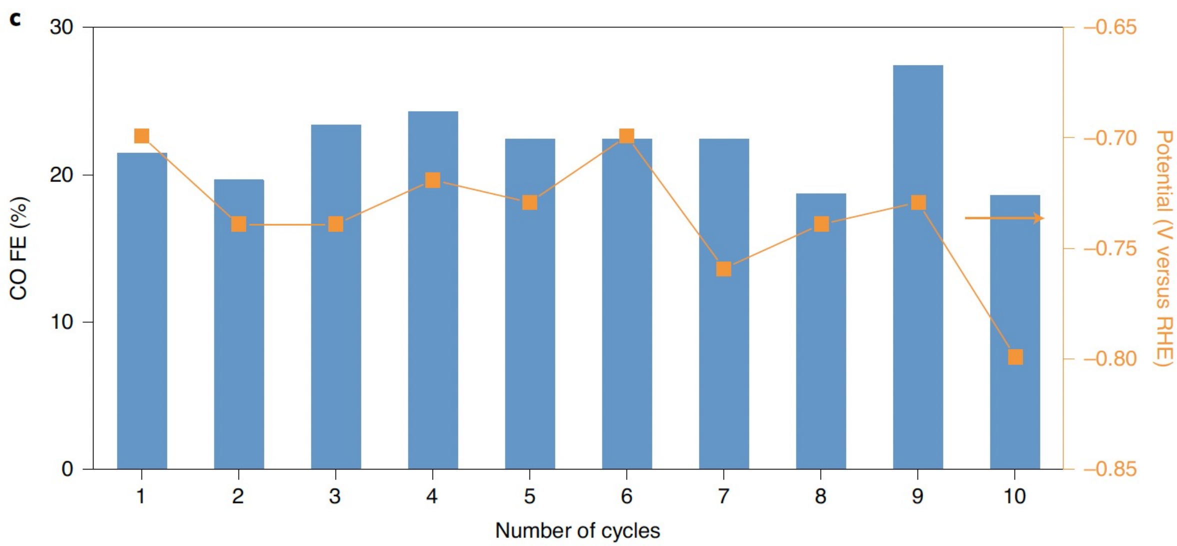
	Achieved
$V_{cathode}$ (V)	-0.8
V_{anode} (V)	0.35
CO Faradaic efficiency (%)	72
Energy efficiency (%)	37
Total energy cost (GJ/ton CO)	24.6



Geonhui Lee, Yuguang C. Li, … Edward Sargent, "Electrochemical upgrade of CO_2 from amine capture solution," Nature Energy, 2021.

1. An early attempt at direct e-upgrade of captured CO_2 to CO

- We performed cycling tests, studying the recyclability of the capture liquid:
  - First we ran amine-CO_2 electrolysis at constant current density, until the concentration of amine-CO_2 was depleted (10 hours)
  - Then, we repurged with CO_2, and initiated a new cycle of electrolysis



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2. In this early attempt … how far were we (at small scale) from $15/GJ? (= 15 GJ/ton)

	Alkaline	Neutral	SOEC	Amine-CO_2 reduction
System	Flow cell	MEA	SOEC	Flow cell
Parameters				
CO_2 utilization (%)	17	35	30	100
Carbonate formation (%)	45	0	0	0
Crossover (%)	2	30	0	0
Exit CO_2 (%)	36	35	70	0
Energy cost (kJ/mole of CO)				
Cathode input	388	388	388	0
Electrolysis	592	640	452	690
Product separation	53	25	58	0
Anode separation	3	21	0	0
Carbonate regeneration	1026	0	0	0
Total energy	**2058**	**1074**	**898**	**690**
Energy cost (GJ/ton CO)				
Total energy	**73.6**	**38.5**	**32.2**	**24.6**

2. In this early attempt … how far were we (at small scale) from \$15/GJ? (= 15 GJ/ton)

- Where does direct-amine CO_2, as achieved in the lab to date, get us?
  - By:
    - Delivering substantially pure CO as the product gas (without CO_2)
    - Avoiding crossover (i.e. avoiding the need to purify the anode stream)
    - Avoiding carbonate loss (or rather, electrically regenerating the capture liquid, rather than needing P/T/V swing)
  - …we achieved 24.6GJ/tonne of CO
    - \$131/tonne of CO for opex

	State-of-the-art			
	Alkaline	**Neutral**	**SOEC**	**Amine-CO_2 reduction**
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3. Where would we have to move the metrics to get to $15/GJ? (= 15 GJ/ton), and how might we approach this?

What would it take to get from 24.6 GJ/ton to 15 GJ ton?

	Achieved	Target
$V_{cathode}$ (V)	-0.8	-0.45
V_{anode} (V)	0.35	0.22
CO Faradaic efficiency (%)	72	92
Energy efficiency (%)	37	60
Total energy cost (GJ/ton CO)	24.6	15

This is demanding!...
The CO_2:MEA adduct is bound to the tune of 35 kJ/mol

- Major efforts to:
  - Reduce voltage
  - Increase FE to CO
  - Increase current density

3. Where would we have to move the metrics to get to $15/GJ? (= 15 GJ/ton), and how might we approach this?

Fuller requirements list for (say) a 3 year study

System	**Capture-to-CO**
EE	60%
Simultaneous with:	
Current density	>300 mA/cm^2 *
Operating time	>100 hours *
Demo	CO_2-loaded electrolyte formed using contactor to air

**Ultimately need*
1-2 A/cm2
10^5 hours

3. Where would we have to move the metrics to get to \$15/GJ? (= 15 GJ/ton), and **how might we approach this?**

Catalyst design: Custom for direct reduction of CO_2:X adducts to Leverage the catalyst-CO2 adducts interaction

Local environment engineering: Control local pH/electrochemical double layer to determine the selectivity

Temperature, Pressure: Tune the mass transport of CO_2 adducts by moderate temperature/elevated pressure

Advanced amines/mixtures: Many degrees of freedom not fully explored in electrochemistry, including the many tried in CO_2 capture

Ionic liquids: task-specific ionic liquids capturing CO2 are active for electrocatalytic conversion

Solid sorbents: Can we tether solid sorbents on a conductive support, and directly reduce from solid-sorbent:CO_2 adduct

4. Grand Problems and Questions

Some challenges:

- CO_2 adduct needs to interact strongly with electrocatalyst surface
  - Can we better tailor the electrochemical double layer?

- Overpotential to break bond energy in CO_2 adducts
  - The strength of binding limits how low can be the overpotential
  - 35 kJ/mole of CO_2 for MEA-CO_2 formation for e.g.
  - Can we further tune the binding, but still get capture with good kinetics?

- The concentration and the diffusivity of capture:CO_2 adduct will affect mass transport
  - Reactions occurs at mass transport limited region

- Electrocatalyst stability in the capture liquid

4. Grand Problems and Questions – Zoomed out further:

How does it work? What is the sequence of steps that lead to CO_2 being reduced from the molecule to which it is adsorbed? Is it reduced *in situ* while still bound in carbamate form?

How well could it work? What determines the limits of current density and overpotential combined? How the system works in coupling with a capture liquid from a capture unit? What is the concentration/impurities range of capture liquid for the direct and upgrade system?

What does it compete with? What are competing reactions, including ones that can emerge at higher applied potentials, and/or after extended reactions? Are the capture molecules at risk of being evaporated/reduced?